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Twinned one-dimensional quasicrystals in Bridgman-grown Al-Si-Cu-Co alloys

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Single grains of $\text{Al}_{60}\text{Si}_2\text{Cu}_{18}\text{Co}_{20}$ with a decaprismatic morphology were grown by the Bridgman method and studied by transmission electron microscopy and x-ray diffraction. Although the diffraction patterns of these grains superficially resemble that of a decagonal quasicrystal, a closer inspection reveals that they are composed of tenfold twins of a one-dimensional quasicrystal along with small domains of three crystalline approximant phases.

I. INTRODUCTION

Since the discovery of an icosahedral quasicrystal in an Al-Mn alloy,¹ a great deal of research has been carried out to study the formation, physical properties, and crystallography of quasicrystals.² Quasicrystals with eightfold,³ tenfold,⁴ and twelvefold⁵ rotational symmetry have also been described. These quasicrystals differ from the icosahedral phase in that they are quasiperiodic in a plane and periodic along the third direction perpendicular to the plane. One-dimensional "Fibonacci"-lattice quasicrystals, periodic in two directions and quasiperiodic along the third, have also been reported.⁶ Although the first generation of quasicrystals were metastable phases, examples of thermodynamically stable icosahedral phases such as Al-Li-Cu,⁷ Al-Cu-*M* (where *M*=Fe, Ru, or Os),⁸⁻¹⁰ as well as decagonal phases of Al-Si-Cu-Co (Refs. 11-14) and Al-Co-Ni (Ref. 15) have allowed the growth of sizable single grains of these alloys for further study.

Of the known decagonal phase alloys the Al-Cu-Co system, with and without minor additions of Si, has recently attracted a great deal of attention. First, large grains up to several centimeters in length, have been produced.¹³ Secondly, several periodicities have been observed along the tenfold axis that are multiples of a fundamental 4-Å periodicity.¹¹ Finally, there appear to be several periodic crystalline approximants to the decagonal phase in this system,¹⁶⁻¹⁸ and it has been suggested that there may be a direct transformation path between the decagonal phase and these crystalline phases.¹⁹

In this paper, we describe studies of single grains of an Al-Si-Cu-Co alloy grown by the Bridgman method in an attempt to produce grains large enough for neutron-scattering measurements (on the order of cubic centimeters). Although the diffraction patterns of these grains superficially resemble that of a decagonal quasicrystal, closer inspection reveals that they are composed of twins of a one-dimensional (1D) quasicrystal along with small domains of three crystalline approximant phases.

II. SAMPLE PREPARATION AND EXPERIMENTS

Single grains with a decaprismatic morphology (Fig. 1) were grown from the $\text{Al}_{60}\text{Si}_2\text{Cu}_{18}\text{Co}_{20}$ alloy by the Bridg-

man method. Raw elements with a purity of 99.99% were arc melted and chill cast into a copper mold. The as-cast ingot was placed in an alumina crucible in the Bridgman apparatus, and heated to 1250°C under a vacuum of 10^{-6} Torr in a Pt-Rh resistance furnace. The furnace was then backfilled with Ar gas to 30 PSI. The crystal-growth rate was approximately 5 mm/h.

Individual grains were separated from the alloy and mounted on an x-ray-precession camera. A zero-layer precession photograph, shown in Fig. 2, taken with the

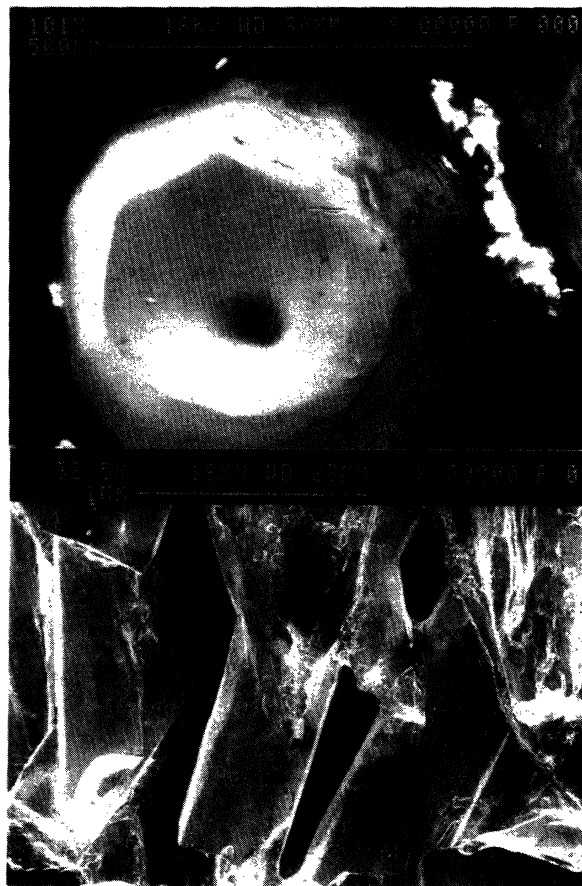


FIG. 1. Scanning electron micrographs of the Al-Si-Cu-Co grains grown by the Bridgman method.

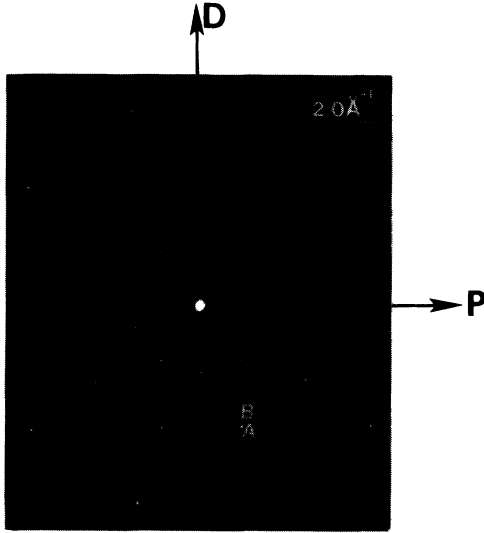


FIG. 2. X-ray-precession photograph taken along the long axis of a single grain. *A* and *B* denote the reflections arising from Mo *K* α and *K* β radiation. The twofold \hat{P} and \hat{D} axes are shown.

long axis of the decaprisim parallel to the incident beam exhibits the tenfold symmetry characteristic of the decagonal phase of $\text{Al}_{62}\text{Si}_3\text{Cu}_{20}\text{Co}_{15}$ reported previously.¹¹ The pairs of spots (i.e., *A* and *B*) correspond to single reflections produced by Mo *K* α and Mo *K* β radiation from the target of the x-ray generator. The streaking arises from the unfiltered brehmsstrahlung radiation from the target. The twofold \hat{P} and \hat{D} directions are marked in Fig. 2.

To verify whether the grains are indeed decagonal phase alloys, a detailed study of peak positions was undertaken using a four-circle diffractometer and Cu *K* α radiation from a rotating-anode x-ray generator. Smaller grains of the sample were also studied by transmission electron microscopy (TEM) selected-area diffraction after polishing and ion milling to the appropriate thickness.

III. RESULTS AND DISCUSSION

The positions of approximately sixty diffraction peaks along the twofold \hat{P} and \hat{D} axes in the tenfold plane were measured to an accuracy of better than $\pm 0.003 \text{ \AA}^{-1}$. Peaks were indexed using a set of basis vectors, which consists of five in-plane vectors along with a sixth perpendicular to the tenfold plane along the periodic direction:

$$\mathbf{q}_j = q_{0p} \left[\cos \left[\frac{j\pi}{5} \right] \hat{D} + \sin \left[\frac{j\pi}{5} \right] \hat{P} \right],$$

$$j = 0 \rightarrow 4,$$

$$\mathbf{q}_5 = q_{0z} \hat{z}.$$

Here, \hat{P} and \hat{D} refer to unit vectors along the *P* and *D* axes of Fig. 2, respectively. The \hat{z} direction is perpendicular to the plane of Fig. 2. The parallel and perpendicular space reciprocal space vectors of diffraction peaks are then defined by

$$\mathbf{G}_{\parallel}^j = \sum_{j=0}^5 \mathbf{q}_j,$$

$$\mathbf{G}_{\perp}^j = \sum_{j=0}^4 \mathbf{q}_{2j \pmod{5}}.$$

The fundamental reciprocal space vectors q_{0p} and q_{0z} have been chosen such that the strongest peaks correspond to reciprocal space vectors with small \mathbf{G}_{\perp} . For our data, $q_{0p} = |\mathbf{G}_{\parallel}(100\,000)| = 0.6360(3) \text{ \AA}^{-1}$ and $q_{0z} = |\mathbf{G}_{\perp}(000\,001)| = 1.525 \text{ \AA}^{-1}$.

In Fig. 3(a) we plot the difference between the experimentally determined and calculated peak positions of diffraction peaks along the \hat{P} and \hat{D} directions, as a function of the phason momentum $|\mathbf{G}_{\perp}|$ of each peak for the decagonal phase, using the indexing scheme described above. For small values of $|\mathbf{G}_{\perp}|$, the difference is within the experimental error. However, with increasing $|\mathbf{G}_{\perp}|$, we find larger and larger differences. Qualitatively, this behavior may be attributed to the presence of anisotropic phason strain. Alternatively, the grain may not be properly classified as a decagonal alloy.

TEM selected-area diffraction (SAD) patterns and high-resolution electron microscopy (HREM) images of

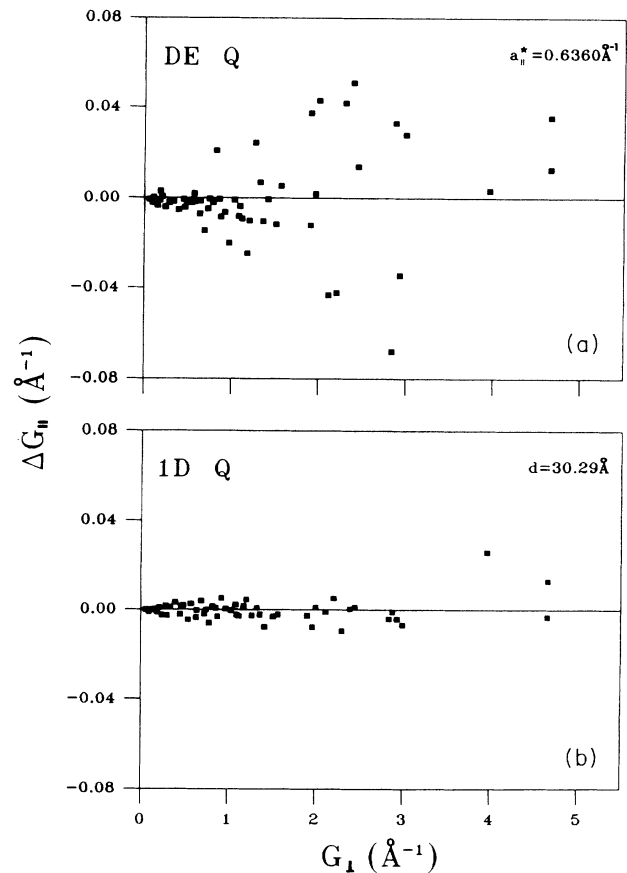


FIG. 3. Difference between the calculated and measured positions of x-ray-diffraction peaks along the \hat{P} and \hat{D} axes as a function of the complementary space reciprocal lattice vector G_{\perp} for (a) the decagonal quasicrystal and (b) the pentagonally twinned 1D quasicrystal.

thinned samples of the alloy reveal a complex microstructure. In contrast to typical electron-diffraction patterns from true decagonal alloys, the SAD pattern, of a one micron region, in Fig. 4 consists of clusters of closely spaced, but clearly distinguishable, reflections characteristic of twinning structures. Indeed, the HREM images in Fig. 5 strongly suggest that the dominant structure consists of twins of a one-dimensional quasicrystal with a spacing along the in-plane periodic direction (the \hat{D} direction in the notation for the decagonal phase) of about 30 Å. The structure along the \hat{P} direction remains quasiperiodic. In Fig. 5(a), five twins oriented at angles of 72° with respect to each other are denoted by arrows. The in-plane periodicity can be clearly seen by viewing the figure along the arrows. An example of a twin boundary with adjacent regions oriented at a relative angle of 72° is also shown in Fig. 5.

We have found that both the x-ray-diffraction peak positions as well as the electron-diffraction patterns may be accounted for by assuming that the dominant phase is a 1D quasicrystal with pentagonally twinned variants. The relationship between the decagonal phase alloys and 1D quasicrystals has been systematically studied by Zhang and Kuo.¹⁹ They have shown that the introduction of an anisotropic linear phason strain field effectively transforms the decagonal phase into the 1D quasicrystal. Starting from the diffraction peak positions for an ideal decagonal quasicrystal, the shifted diffraction peak positions for a single twin may be written as

$$\mathbf{G}'_{\parallel} = \mathbf{G}_{\parallel} + \vec{\mathbf{M}} \cdot \mathbf{G}_{\perp},$$

where $\vec{\mathbf{M}}$ is a second-rank tensor. For the case at hand we find that

$$\vec{\mathbf{M}} = \begin{bmatrix} -0.021 & 0 \\ 0 & 0 \end{bmatrix},$$

resulting in a diffraction pattern that retains its quasiperiodicity along the \hat{P} direction but has a periodic repeat distance along the \hat{D} direction of 30.29 Å. Combin-

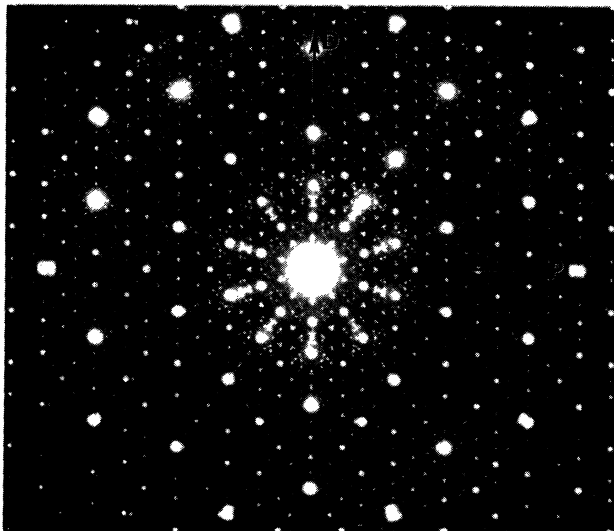


FIG. 4. Selected-area diffraction pattern taken along the pseudotenfold axis of the sample.

ing five of these twins at a relative orientation of 72° results in the simulated electron-diffraction pattern of Fig. 6(a), which is in very good agreement with the experimental pattern. Furthermore, as shown in Fig. 3(b), the predicted shifts in the x-ray-diffraction peak positions result in a significantly better match with experiment.

Small regions of at least three crystalline approximants marked as C1, C2, and C3 in Fig. 5 are also observed. The lattice parameters and rhombic angles for these structures are 31.85 Å and 72°, 51.53 Å and 36°, and 51.53 Å and 72°, respectively. Both the C1 and C2 structures have previously been identified as crystalline approximants to the decagonal phase of Al-Cu-Co by Lau-nois *et al.*¹⁶ Since some small regions of crystallinity are observed in the HREM micrographs, it is useful to compare the calculated SAD patterns for these structures

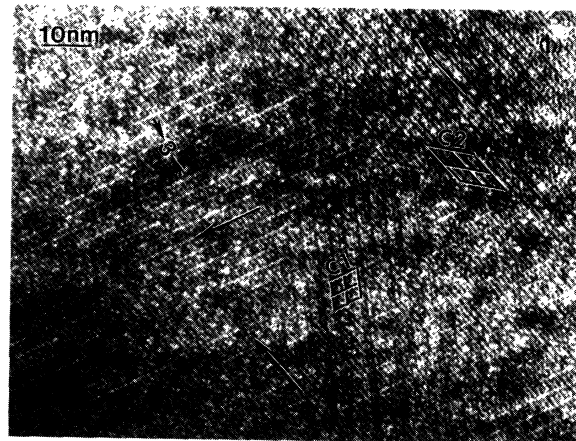
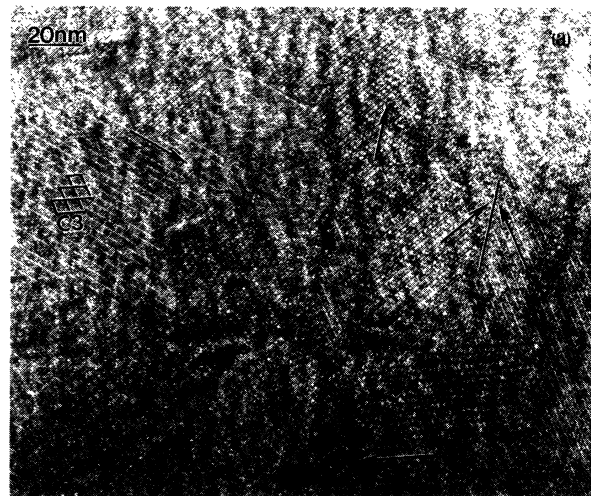


FIG. 5. (a) HREM micrograph with the incident electron beam being parallel to the tenfold axis. Most of the area has only one-dimensional periodicity and the boundary of these 1D quasicrystals are very clear. The 1D periodicity will be observed more easily if you look at the picture along the arrows. The crystalline phase C3 is found in here also. (b) HREM micrograph taken under the same conditions as above, but over a different region of the sample. The crystalline phases C1 and C2 are found in here, however, the one-dimensional quasicrystal remains the major phase.

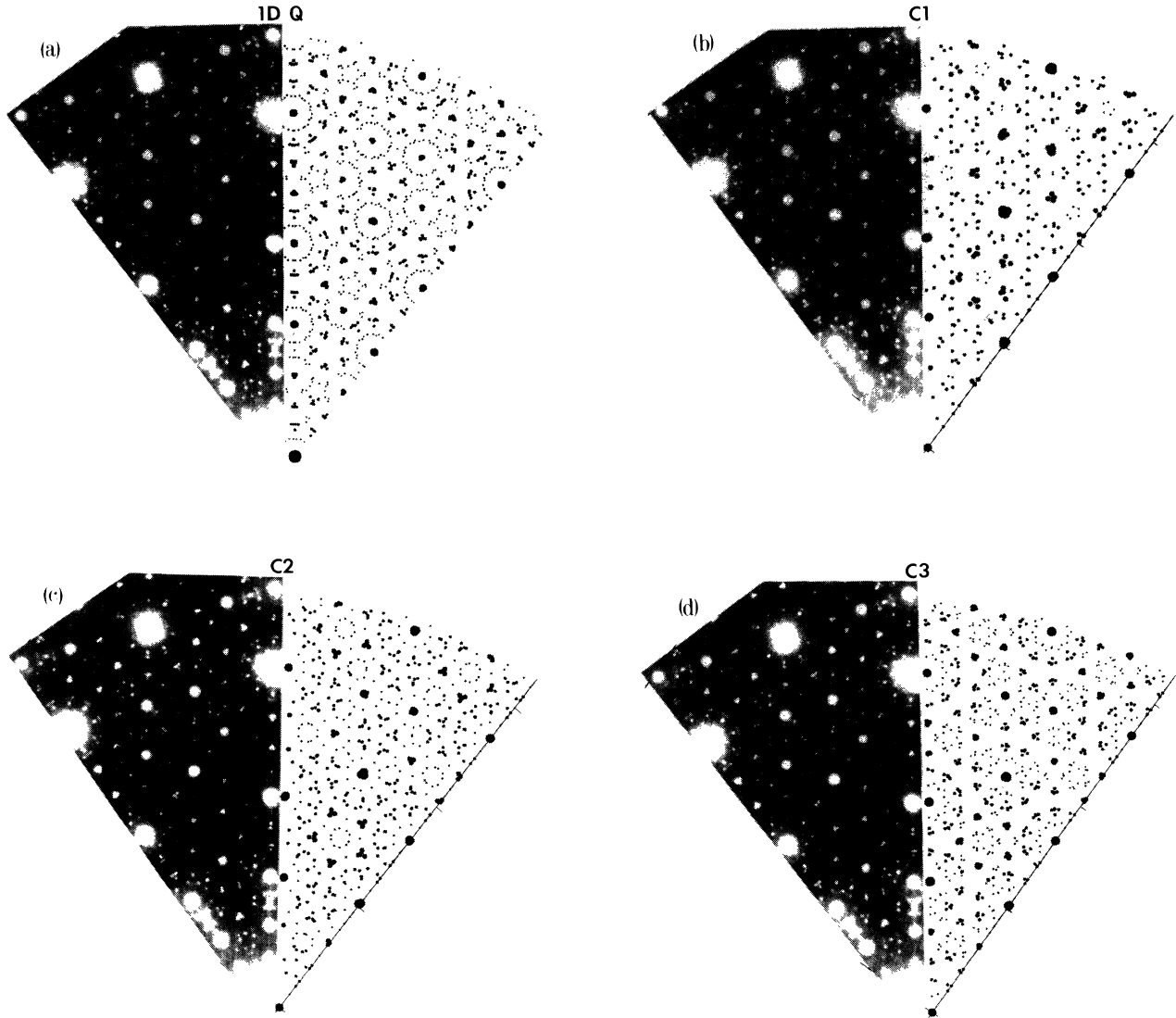


FIG. 6. A comparison between the experimental and calculated SAD patterns for twinning of (a) 1D quasicrystal; (b) C1, (c) C2, and (d) C3.

with the experimental results. The simulated SAD patterns from the appropriate set of twins of C1, C2, and C3, shown in Figs. 6(b)–6(d) show that only C3 finds reasonable agreement with the experimental SAD pattern, although the match with the pattern calculated for the twinned one-dimensional quasicrystal Fig. 6(a) is somewhat better. We conclude that the dominant phase of the Bridgman-grown Al-Si-Cu-Co alloy is the 1D quasicrystal.

IV. CONCLUSIONS

It was recently noted by Daulton and Kelton¹⁷ that the decagonal phase of Al-Si-Cu-Co, for Si compositions less

than 2.5%, produces electron-diffraction spots with pronounced triangular anisotropy. Previous explanations for the spot anisotropy have ranged from the presence of anisotropic linear phason strain²⁰ to the presence of coherently oriented twins of periodic crystalline phases. Here we find that the triangular spots may be quantitatively accounted for by the presence of twinned one-dimensional quasicrystals.

The one-dimensional quasicrystal in this alloy may be directly obtained from the decagonal phase alloy through the appropriately defined anisotropic linear phason strain (the tensor \vec{M} described above), as originally proposed by Zhang and Kuo.¹⁹ We also point out that the other crystalline phases in this sample (C1, C2, and C3) can also be related to the decagonal phase upon application of the

appropriate phason strain tensor, since they are periodic approximants to the decagonal phase. Indeed it appears that the one-dimensional quasicrystal in Al-Si-Cu-Co may be an intermediate phase that provides a link between the decagonal quasicrystal and periodic crystalline phases.

ACKNOWLEDGMENTS

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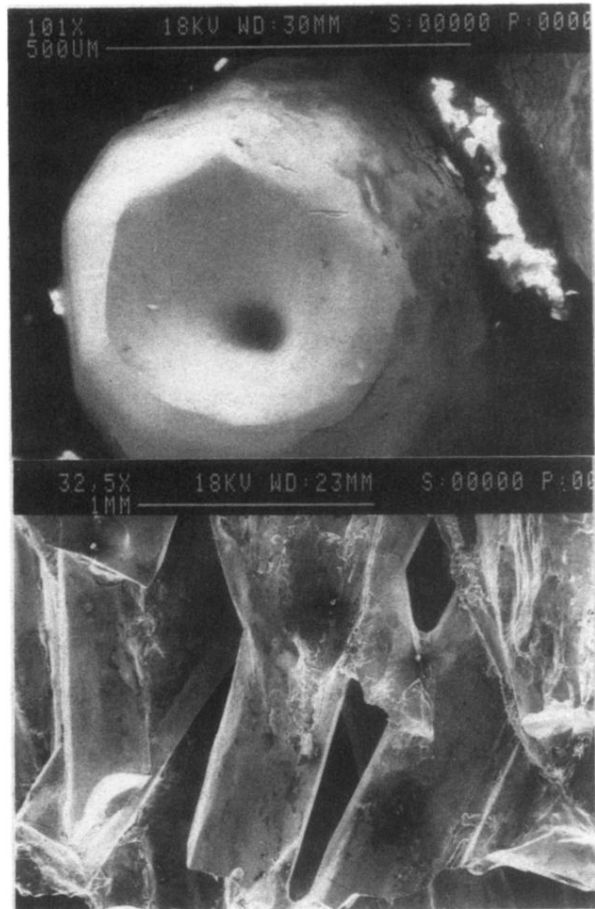


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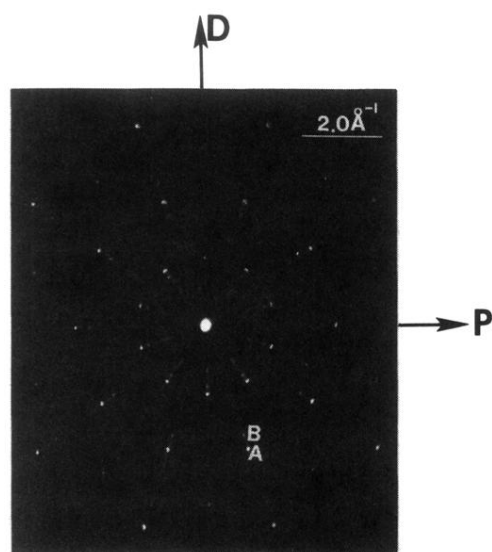


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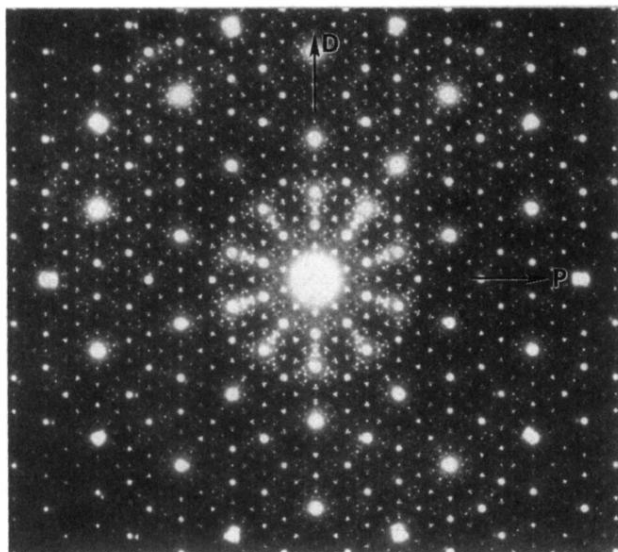


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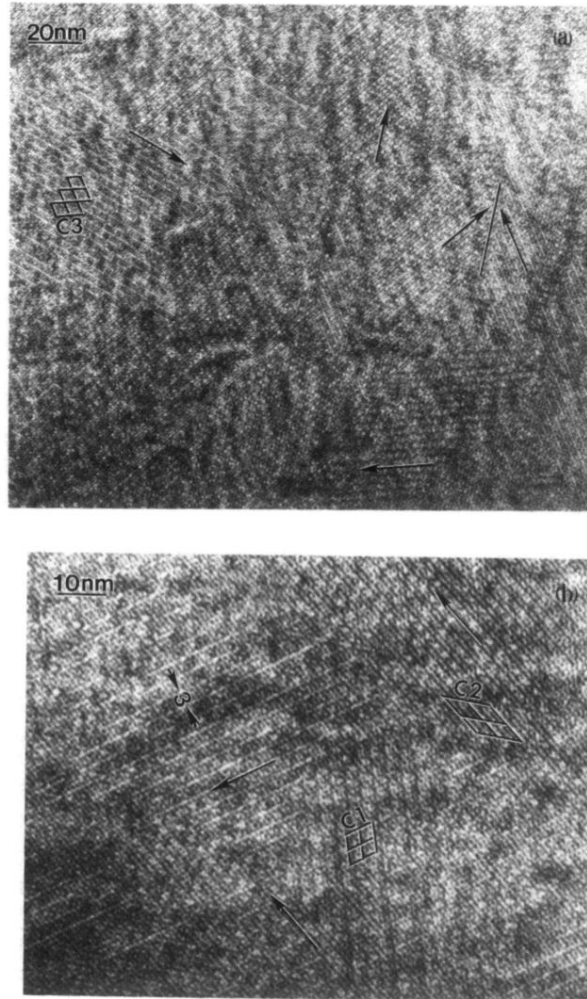


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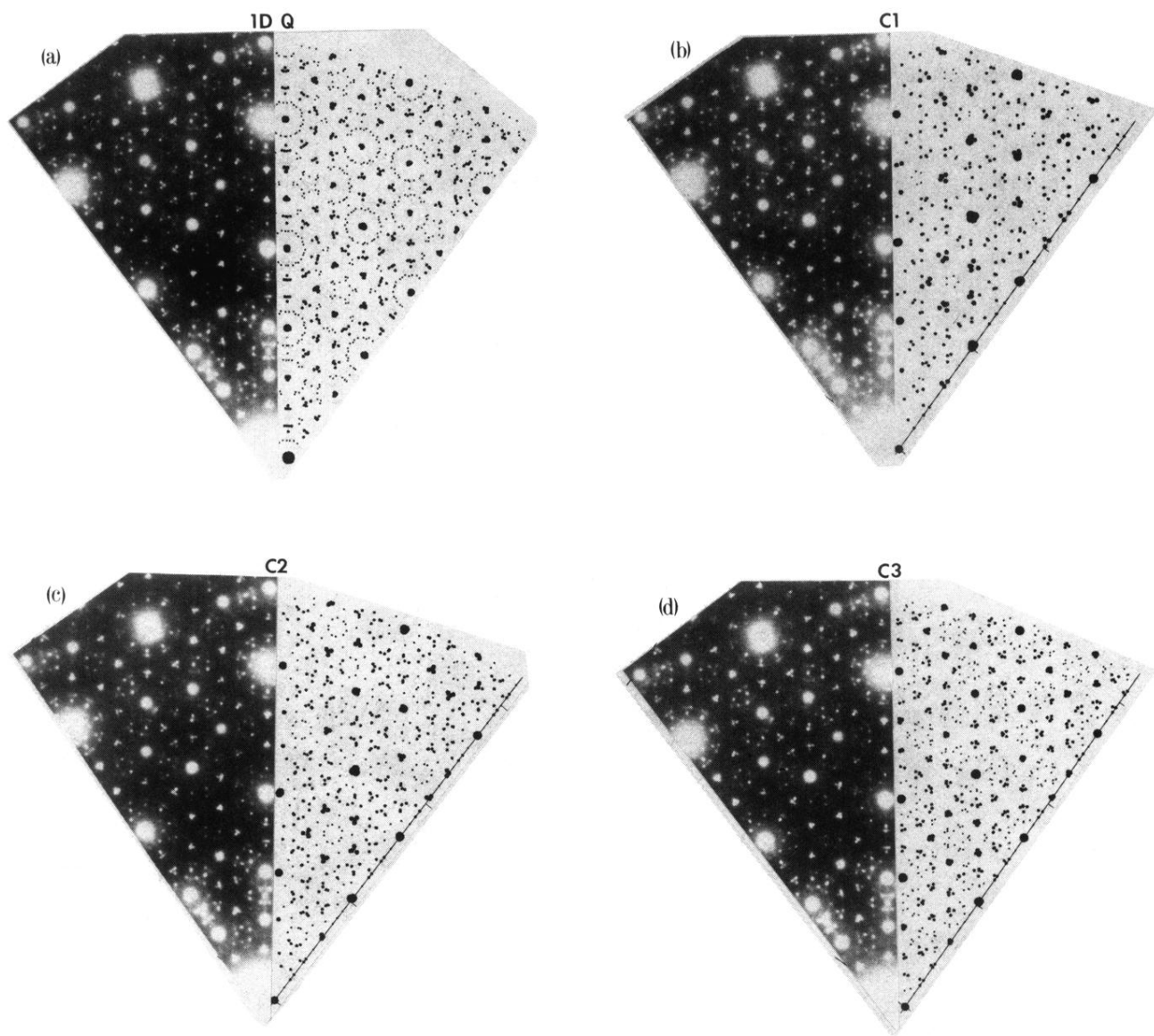


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